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Spectroscopic Characterization of Electrophilic d⁴ Methylene and Benzyldiene Complexes of the Type Cp(CO)₂(L)M=CHR⁺ (L = PPh₃, PEt₃; M = Mo, W; R = H, Ph). Experimental Determination of Barriers to Rotation about the Tungsten-Methylene Multiple Bond¹

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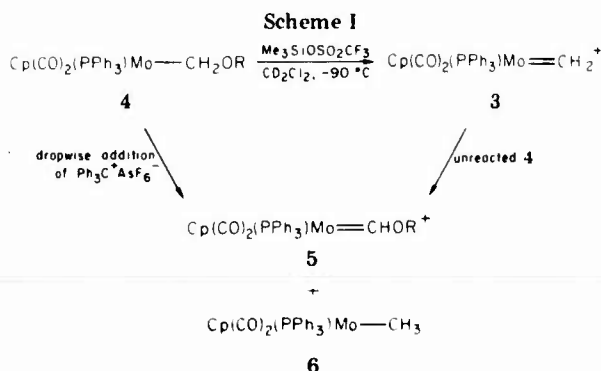
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Summary: The first spectrally characterized examples of nonheteroatom-stabilized carbene complexes of the type Cp(CO)₂LM=CHR⁺ (L = PPh₃, PEt₃; M = Mo, W; R = H, Ph) are reported. The parent methylene complexes **2a** (M = W, L = PPh₃) and **2b** (M = W, L = PEt₃) and the benzyldiene complex **2c** (M = W, L = PPh₃) are synthesized by hydride abstraction from the alkyl complexes Cp(L)(CO)₂WCH₂R (R = H, Ph) using Ph₃C⁺AsF₆⁻.

The chemistry of d⁶ electrophilic carbene complexes of the general type CpL₂M=CRR' is rapidly developing, and a variety of both heteroatom and nonheteroatom-stabilized species is now known. Several structures have

been examined crystallographically,² while both structure and dynamics have been scrutinized spectroscopically and theoretically.³⁻⁶ The more electrophilic species exhibit high reactivity toward nucleophilic reagents.^{3c,4-8} In contrast, relatively few electrophilic carbene complexes in the parallel d⁴ series with general structure CpL₂M=CRR' have been studied. Isolable or spectroscopically characterized examples include only heteroatom-stabilized complexes: for example, Cp(CO)₂(Ph₃M)M' = Cr(OR') (M = Sn, Ge; M' = Mo, W; R = CH₃, C₆H₅),⁹ Cp(CO)₂(PPh₃)-Mo=C(CH₃)(OCH₃)⁺,¹⁰ Cp(CO)₂LMo=CRR' (L = CO, PPh₃; R = F, C₂F₅),¹¹ Cp(CO)₂(PPh₃)-Mo=CCH₂CH₂CH₂O⁺,¹² and Cp(CO)₂W=C(NEt₂)CH-(CH₃)CO.¹³ No nonheteroatom-stabilized species have been well characterized.¹⁴

We describe here the facile synthesis and spectral characterization of the d⁴ cationic methylene complexes in the series Cp(CO)₂LM=CH₂⁺ (L = PEt₃, PPh₃; M = Mo, W) and the benzyldiene complex Cp(CO)₂(PPh₃)-



(1) This work was presented in part at the 181st National Meeting of the American Chemical Society, Atlanta, GA, April 1981, "Abstracts of Papers", American Chemical Society: Washington, DC, 1981; INORG 170.

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- (14) (a) The methylene species Cp(CO)₃Mo=CH₂⁺ has been postulated as an intermediate in the acid-induced ionization of the α-ether Cp(CO)₃Mo-CH₂OCH₃ (Gross, M. L. H.; Loh, M.; Whiteley, R. N. *J. Chem. Soc. A* 1967, 1508. (b) Similarly, Me₃SiOSO₂CF₃ reacts with Cp(CO)₃W-CH₂OCH₃ at low temperatures to precipitate Cp(CO)₃W-CH₂OSO₂CF₃ which reacts with a variety of nucleophiles (X⁻) to yield complexes of the type Cp(CO)₃W-CH₂X (Beck, W. A.; Schlöter, K.; Ernst, H. Ninth International Conference on Organometallic Chemistry, Sept 1979, Dijon, France; Abstract No. C53). No spectroscopic data related to these methylene complexes have been reported.

Table I. ^1H NMR Data for $[\text{Cp}(\text{CO})_2(\text{L})\text{M}=\text{CHR}]^+\text{AsF}_6^-$ Complexes in CD_2Cl_2 ^a

complex	T, °C	$\delta(\text{Cp})$	$\delta(\text{H}_a, \text{H}_b)$
$[\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{MoCH}_2]^+\text{OSO}_2\text{CF}_3^-$ (3)	90	5.84 (d, $J_{\text{P-H}} = 1.2$ Hz)	H_a, H_b 15.4 (d, $J_{\text{P-H}} = 12.5$ Hz)
$[\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{WCH}_2]^+\text{AsF}_6^-$ (2a)	110	5.93 (d, $J_{\text{P-H}}$ ca. 1 Hz)	H_a 14.2 (br) H_b 16.0 (d, $J_{\text{P-H}} = 24$ Hz)
$[\text{Cp}(\text{CO})_2(\text{PET}_3)\text{WCH}_2]^+\text{AsF}_6^-$ (2b)	50 110	6.04 (d, $J_{\text{P-H}}$ ca. 1 Hz)	H_a, H_b 15.1 (d, $J_{\text{P-H}} = 16.2$ Hz) H_a 13.9 (apparent t, $J = \text{ca. } 7$ Hz) ^c H_b 15.5 (dd, $J_{\text{H-H}} = 5$ Hz, $J_{\text{P-H}} = 24$ Hz)
$[\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{WCHPh}]^+\text{AsF}_6^-$ (2c)	40 +20	5.97 (d, $J_{\text{P-H}} = 1.6$ Hz)	H_a, H_b 14.8 (d, $J_{\text{P-H}} = 16.2$ Hz) H_a 14.1 (d, $J_{\text{P-H}} = 4.9$ Hz)

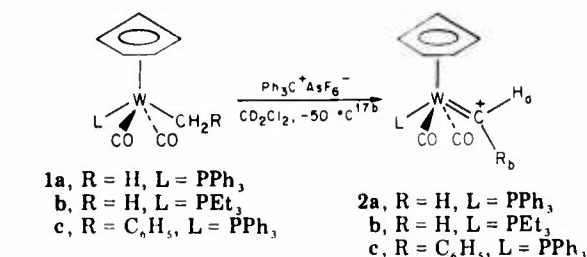
^a NMR data for the carbene complexes were obtained at 250.13 MHz. Shifts are referenced to CHDCl_2 , taken as δ 5.32. All aromatic resonances are observed in the δ 7–8 range and, with the exception of 5, are overlapped by Ph_3CH . ^b ^1H NMR (PET_3) δ 1.8 (m, 6 H, PCH_2CH_3), 1.04 (m, 9 H, PCH_3CH_3). ^c The apparent triplet is a result of the near equivalence of $J_{\text{P-H}}$ and $J_{\text{H-H}}$. Because of viscosity broadening, only approximate values were obtainable. ^d ^{183}W satellites can be observed for H_a , $J_{\text{W-H}} = 6.9$ Hz.

Table II. ^{13}C NMR of $[\text{Cp}(\text{CO})_2(\text{L})\text{W}=\text{CHR}]^+\text{AsF}_6^-$ Complexes in CD_2Cl_2 ^a

complex	$\delta(\text{Cp})$	$\delta(\text{carbene})$	$\delta(\text{CO})$
$[\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{WCH}_2]^+\text{AsF}_6^-$ (2a)	99.7 (s)	303.6 (br)	207.6 (d, $J_{\text{P-C}} = 21.5$ Hz)
$[\text{Cp}(\text{CO})_2(\text{PET}_3)\text{WCH}_2]^+\text{AsF}_6^-$ (2b)	98.5 (s)	296.8 (br)	206.4 (d, $J_{\text{P-C}} = 21.4$ Hz)
$[\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{WCHPh}]^+\text{AsF}_6^-$ (2c)	99.7 (d, $J_{\text{C-H}} = 183$ Hz)	299.8 (br, d, $J_{\text{C-H}} = 138$ Hz)	214.1 (d, $J_{\text{P-C}} = 16.8$ Hz)

^a Proton noise-decoupled spectra were obtained at 62.89 MHz. Shifts referenced to CD_2Cl_2 at 53.8 ppm. All aromatic resonances were observed in the δ 125–150 range and are overlapped by $\text{Ph}_3\text{C-H}$. ^b ^{13}C NMR (PET_3): δ 19.4 (d, $J_{\text{P-C}} = 30.5$ Hz, PCH_2CH_3), 8.1 (d, $J_{\text{P-C}} = 5.4$ Hz, PCH_3CH_3). ^c Coupled spectrum obtained.

$\text{W}=\text{CHPh}$.¹⁵ Treatment of the readily prepared tungsten alkyl complexes **1a–c**¹⁶ with 1 equiv of trityl hexafluoroarsenate in methylene chloride at -50°C leads to quantitative generation of the cationic alkylidene species **2a–c**.¹⁷ The ^{13}C and ^1H NMR data for these complexes are summarized in Tables I and II. The characteristic low-field ^1H resonances for the hydrogen(s) attached directly to the carbene carbon, and ^{13}C resonances of the carbene carbon atom are clearly indicative of the carbene structure. These shift values compare closely with those for analogous electrophilic d⁶ complexes.^{3–4}



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The molybdenum methylene complex, $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{Mo}=\text{CH}_2^+$, **3**, is generated by the reaction of ether precursors $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{Mo}-\text{CH}_2\text{OR}$, **4** (R = CH_3 , CH_2Ph , $\text{COC}(\text{CH}_3)_3$),^{14b,16b,18} with $(\text{CH}_3)_3\text{SiOSO}_2\text{CF}_3$ at -90°C

$^\circ\text{C}$ in CD_2Cl_2 . Quantitative generation of **3** is difficult and samples of **3** are normally contaminated with small amounts of the heteroatom carbene, **5**, and the methylene complex, **6**, due to hydride transfer from **4** to **3**¹⁹ (see Scheme I). Indeed, when trityl hexafluoroarsenate is added dropwise to solutions of **4** in CD_2Cl_2 (-90°C), no methylene complex can be detected. Instead complexes **5** and **6** are generated in equimolar amounts. A similar reaction has been observed between $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}=\text{CH}_2\text{OCH}_3$ and $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}=\text{CH}_2^+$.^{4a}

Complex **3** decomposes rapidly above -70°C by disproportionation to $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{Mo}(\text{C}_2\text{H}_4)^+$ and $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{Mo}^+$, the latter presumed to be stabilized by coordination to a solvent molecule or the triflate counterion.^{20b} The same mode of decomposition is observed for the tungsten methylene complexes above -20°C ($t_{1/2}$ (-20°C) ca. 2 h).²⁰ In contrast, the tungsten benzylidene complex **2c** is stable in CD_2Cl_2 solution at room temperature in a sealed tube for long periods of time. At 50°C , decomposition occurs with $t_{1/2}$ ca. 15 h, but no decomposition products could be characterized. The benzylidene complex can be isolated as an air-stable green hexafluoroarsenate salt in nearly quantitative yield by precipitation from a CH_2Cl_2 solution with hexane at 0°C .

The nonequivalence of the methylene hydrogens in the tungsten complexes **2a,b** confirms that the methylene

(15) An X-ray crystallographic study of a neutral d⁴ benzylidene complex $\text{Cp}_2\text{W}=\text{CHPh}$ has recently been reported (Caulton, K. G.; Marsella, J. A.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* 1981, 103, 5596).

(16) (a) ^1H NMR (CDCl_3): $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{W}-\text{CH}_3$, δ 0.50 (d, $J_{\text{P-H}} = 2.4$ Hz, 3 H, CH_3), 4.79 (d, $J_{\text{P-H}} = 1.8$ Hz, 5 H, Cp), 7–8 (m, 15 H, Ph); $\text{Cp}(\text{CO})_2(\text{PET}_3)\text{W}-\text{CH}_3$, δ 0.37 (d, $J_{\text{P-H}} = 2.6$ Hz, 3 H, CH_3), 1.04 (m, 9 H, PCH_2CH_3), 1.8 (m, 6 H, PCH_3CH_3), 4.95 (d, $J_{\text{P-H}} = 1.5$ Hz, 5 H, Cp); $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{W}-\text{CH}_2\text{Ph}$, δ 3.06 (d, $J_{\text{P-H}} = 2.8$ Hz, 2 H, CH_2Ph), 4.76 (d, $J_{\text{P-H}} = 1.8$ Hz, 5 H, Cp), 7–8 (m, 20 H, Ph). (b) The Mo and W carbene precursors were determined to be the trans isomers by the observation of a single ^{13}C resonance in each case, indicating equivalence of the carbonyls. (c) **1a–c** were prepared by reaction of $\text{Cp}(\text{CO})_2\text{LW}^-$ with methyl iodide or benzyl chloride.

(17) (a) Complex **2a** can also be generated by dropwise addition of $\text{Ph}_3\text{C}^+\text{AsF}_6^-$ in CD_2Cl_2 to the α -ether $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{W}-\text{CH}_2\text{OCH}_2\text{Ph}$ in CD_2Cl_2 at -78°C . (b) The generation of **2c** was carried out at 0°C .

(18) ^1H NMR (CDCl_3): $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{Mo}-\text{CH}_2\text{OCH}_3$, δ 3.37 (s, 3 H, CH_3), 4.75 (d, $J_{\text{P-H}} = 3.6$ Hz, 2 H, CH_2), 4.85 (d, $J_{\text{P-H}} = 1.6$ Hz, 5 H, Cp), 7–8 (m, 15 H, Ph); $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{Mo}-\text{CH}_2\text{OCH}_2\text{Ph}$, δ 4.54 (d, $J_{\text{P-H}} = 3.7$ Hz, 2 H, $\text{W}-\text{CH}_2$), 4.83 (d, $J_{\text{P-H}} = 1.8$ Hz, 5 H, Cp), 5.29 (s, 2 H, CH_2Ph), 7–8 (m, 20 H, Ph); $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{Mo}-\text{CH}_2\text{OCOC}(\text{CH}_3)_3$, δ 1.21 (s, 9 H, t-Bu), 4.87 (d, $J_{\text{P-H}} = 1.8$ Hz, 5 H, Cp), 5.55 (d, $J_{\text{P-H}} = 3.8$ Hz, 2 H, CH_2), 7–8 (m, 15 H, Ph).

(19) ^1H NMR (CD_2Cl_2): $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{Mo}=\text{CH}(\text{OCH}_3)^+\text{OSO}_2\text{CF}_3^-$, δ 4.58 (s, 3 H, OCH_3), 5.56 (d, $J_{\text{P-H}} = 1.2$ Hz, 5 H, Cp), 7–8 (m, 15 H, Ph), 12.10 (s, 1 H, carbene proton); $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{Mo}-\text{CH}_3$, δ 0.34 (d, $J_{\text{P-H}} = 3.2$ Hz, 3 H, CH_3), 4.70 (d, $J_{\text{P-H}} = 1.6$ Hz, 5 H, Cp), 7–8 (m, 15 H, Ph).

(20) (a) The identity of the ethylene complexes $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{Mo}(\text{C}_2\text{H}_4)^+\text{AsF}_6^-$ and $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{W}(\text{C}_2\text{H}_4)^+\text{AsF}_6^-$ was verified by independent synthesis from the reaction of $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{M}-\text{CH}_2\text{CH}_3$ with $\text{Ph}_3\text{C}^+\text{AsF}_6^-$. ^1H NMR (CD_2Cl_2) $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{Mo}(\text{C}_2\text{H}_4)^+\text{AsF}_6^-$, δ 3.53 (d, $J_{\text{P-H}} = 1.8$ Hz, 4 H, C_2H_4), 5.28 (d, $J_{\text{P-H}} = 1.5$ Hz, 5 H, Cp), 7–8 (m, 15 H, Ph); $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{W}(\text{C}_2\text{H}_4)^+\text{AsF}_6^-$, δ 3.28 (d, $J_{\text{P-H}} = 2.4$ Hz, 4 H, C_2H_4), 5.36 (d, $J_{\text{P-H}} = 2.0$ Hz, 5 H, Cp), 7–8 (m, 15 H, Ph); $\text{Cp}(\text{CO})_2(\text{PET}_3)\text{W}(\text{C}_2\text{H}_4)^+\text{AsF}_6^-$, δ 1–2 (m, 15 H, PET_3), 3.02 (d, $J_{\text{P-H}} = 2.8$ Hz, 4 H, C_2H_4), 5.36 (d, $J_{\text{P-H}} = 1.2$ Hz, 5 H, Cp). (b) Upon decomposition of **2a** and **2b**, Cp signals at δ 5.79 (**2a**) and δ 5.86 (**2b**) appear simultaneously with the Cp signals for the ethylene complexes $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{W}(\text{C}_2\text{H}_4)^+$ or $\text{Cp}(\text{CO})_2(\text{PET}_3)\text{W}(\text{C}_2\text{H}_4)^+$. Similarly, in the decomposition of $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{Mo}=\text{CH}_2^+$ a Cp signal at δ 5.65 appears together with the Cp signal for the ethylene complex $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{Mo}(\text{C}_2\text{H}_4)^+$. In analogy with Beck's observation of $\text{Cp}(\text{CO})_2\text{M}^+$ (M = Mo, W) coordinated to either BF_4^- , PF_6^- , or CH_2Cl_2 (Beck, W. A.; Schlöter, K. Z. *Naturforsch. B. Anorg. Chem. Org. Chem.* 1978, 33B, 1214), we assume these signals are due to solvent or counterion coordinated $\text{Cp}(\text{CO})_2\text{LM}^+$.

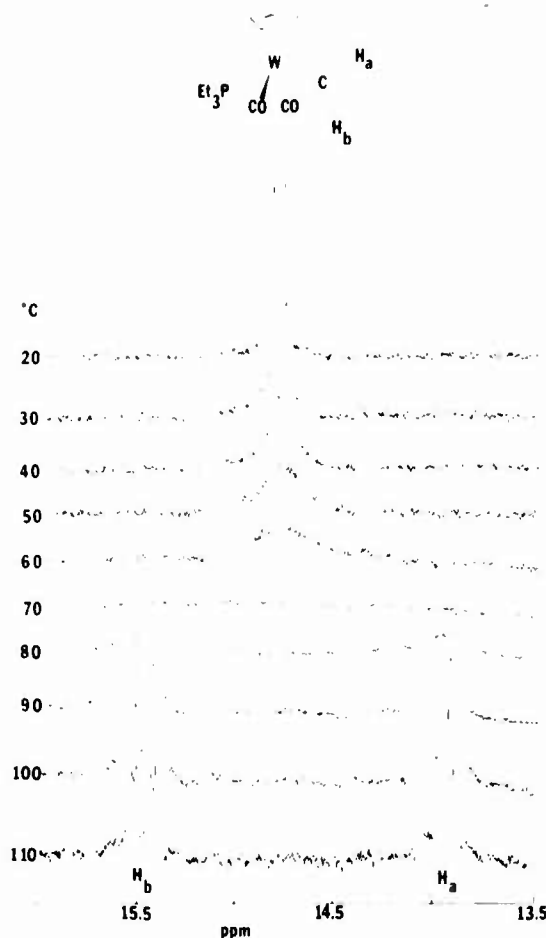


Figure 1. Variable-temperature 250-MHz ^1H NMR of $\text{Cp}(\text{CO})_2(\text{PEt}_3)\text{W}=\text{CH}_2^+$ in CD_2Cl_2 .

moiety adopts the "upright" conformation with the H_a -C- H_b plane aligned with the W-P bond. Using extended Hückel calculations for the similar system $\text{Cp}(\text{CO})_2(\text{PH}_3)\text{Mo}=\text{CH}_2^+$, Hoffmann²¹ has predicted such a ground-state conformation, with a calculated barrier to rotation around the Mo=C bond of 15 kcal/mol. The upright conformation is also that observed by X-ray crystallography for the structurally similar heteroatom carbenes, $\text{Cp}(\text{CO})_2(\text{Ph}_3\text{M})\text{M}'=\text{CR}(\text{OR}')$.⁹ The assignment of H_a resonances to the synclinal hydrogen is based on the close comparison of the chemical shifts and ^{31}P - ^1H coupling constants to those in the benzylidene complex 2c. In 2c the aryl ring is assumed to be in the sterically less crowded anticlinal position. Thus the benzylidene hydrogen occupies the synclinal position.

The ^1H NMR spectra of both tungsten methylene complexes 2a and 2b are temperature dependent and allow

calculation of the barrier to rotation around the tungsten-carbon multiple bond (see Figure 1). As the temperature is raised above -110°C , the two resonances for the nonequivalent methylene hydrogens begin to broaden. Coalescence for 2a occurs at -85°C (250 MHz) and for 2b at -70°C (250 MHz). Each spectrum sharpens to a doublet above -40°C . Line-shape analysis yields free energies of activation, ΔG^\ddagger , for bond rotation of 8.3 ± 0.1 kcal/mol for 2a and 9.0 ± 0.1 kcal/mol for 2b. The higher barrier for 2b is consistent with the better donor properties of Et_3P relative to PPh_3 .

For the molybdenum methylene complex, 3, only a two-proton doublet (δ 15.4 ($J_{\text{P-H}} = 12.5$ Hz)) can be observed even at temperatures as low as -90°C . The similarity of the chemical shift and $J_{\text{P-H}}$ to those observed for the high-temperature averaged spectra of 2a (δ 15.1 ($J_{\text{P-H}} = 16.2$ Hz)) and 2b (δ 14.8 ($J_{\text{P-H}} = 16.2$ Hz)) suggests that the molybdenum complex also adopts the upright conformation, but that the rotational barrier is quite low. With the use of the high-temperature approximation formula to obtain a minimum rate constant for the exchange, a conservative upper limit to the rotational barrier can be set at 6.7 kcal/mol.²² The observed values of $\Delta G^\ddagger_{\text{rot}}$ for the Mo and W methylene complexes are somewhat lower than those of the $\text{Cp}(\text{diphos})\text{Fe}=\text{CH}_2^+$ system ($\Delta G^\ddagger_{\text{rot}} = 10.4$ kcal/mol)^{3d} and considerably lower than the $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}=\text{CH}_2^+$ system whose nonequivalent methylene signals remain sharp to 10°C ($\Delta G^\ddagger_{\text{rot}} \geq \text{ca. } 15$ kcal/mol).^{4a}

The high electrophilicity of these complexes is substantiated by their observed reactivity with olefins. Transfer of the methylene moiety of 2a, 2b and 3 to styrene in CH_2Cl_2 occurs within 10–15 min at -78°C to produce phenylcyclopropane in $> 50\%$ yields. On the basis of these results, the readily generated and easily modified $\text{Cp}(\text{CO})_2\text{LM}=\text{CHR}^+$ systems appear to have potential as carbene-transfer reagents. Synthetic modifications of these complexes as well as reactions with other nucleophilic and unsaturated organic substrates are currently under investigation.

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(21) Hoffman, R.; Kubáček, P.; Havlas, Z. *Organometallics* 1992, 11, 180.

(22) Line broadening of the methylene signal of 3 is ca. 8.8 Hz at half-height (ΔW) at -90°C (broadening may be viscosity related). Assuming the chemical shift difference, $\nu_A - \nu_X$, in the static spectrum will be similar to that for the tungsten species 2a (458 Hz) and applying the high-temperature approximation $k = (\nu_A - \nu_X)^2 / 2(\Delta W)$, we can estimate the minimum rate constant for exchange at -90°C as $3.64 \times 10^4 \text{ s}^{-1}$ ($\Delta G^\ddagger_{\text{rot}} \leq 6.7$ kcal/mol).

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